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Optical Properties of Irradiated LiF Crystals in the Extreme Ultraviolet

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Optical absorptions of LiF crystals irradiated with γ-rays or Van de Graaff electrons have been investigated in the extreme ultraviolet region. A new absorption band at 11.1 ev was found at the tail of fundamental absorption band. The oscillator strength of the band is estimated to be about 0.25 on the assumption of one electron center. Behaviors of other absorptions which were observed in the process of light bleaching of F band are also described and discussions are given on the nature of 222 mμ band.

INTRODUCTION

Many interests have been taken in the properties of LiF crystal, because the electron configurations of its constituent ions are simple and it shows somewhat different behaviors from other alkalihalides. For the study of color centers several methods of coloration (additive and electrolytic colorations as well as the coloration by the irradiation of ionizing radiation) are applied to most alkalihalides. For LiF, however, only the irradiating coloration has been realized up to the present.

Pringsheim *et al*[1] already investigated the optical and electrical properties of LiF crystals irradiated with x-rays or Van de Graaff electrons in the range of wavelength longer than 2000 Å. On the other hand optical data in the extreme ultraviolet are few, for the lack of an appropriate vacuum spectrophotometry until recently and because of difficulties in growing pure LiF crystal.

Present paper gives absorption spectra in the extreme ultraviolet on LiF single crystals irradiated with γ-rays or Van de Graaff electrons and describes some relations to the results[1] hitherto obtained.

EXPERIMENTAL PROCEDURES

LiF single crystals used in this experiment were obtained from the Harshaw Chem. Co. and were kindly offered by Prof. Pringsheim previously. They were found the purest among those available by the measurement of absorptions near the tail of fundamental band.

Irradiations of specimens with γ-rays from Co^{60} were done at room temperature at the Institute for Chemical Research in this University. Bombardments with 0.9 Mev electrons from a Van de Graaff machine were performed at room temperature and at -70°C by the facilities of the Research Department of Toyo Rayon Co. Optical

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absorptions were measured at room temperature by a vacuum spectrophotometer[2] of Seya-Namioka type constructed in this laboratory. For the light bleaching of F band specimens were exposed to light of 2537 Å from a mercury lamp filtered through a Corning red purple filter.

RESULTS AND DISCUSSIONS

Fig. 1 shows absorption spectra of LiF crystals irradiated with γ-rays or 0.9 Mev electrons. Specimen 2 was found to have an absorption band at 11.1 ev well separated from the fundamental band as seen in the figure. The band seemed to

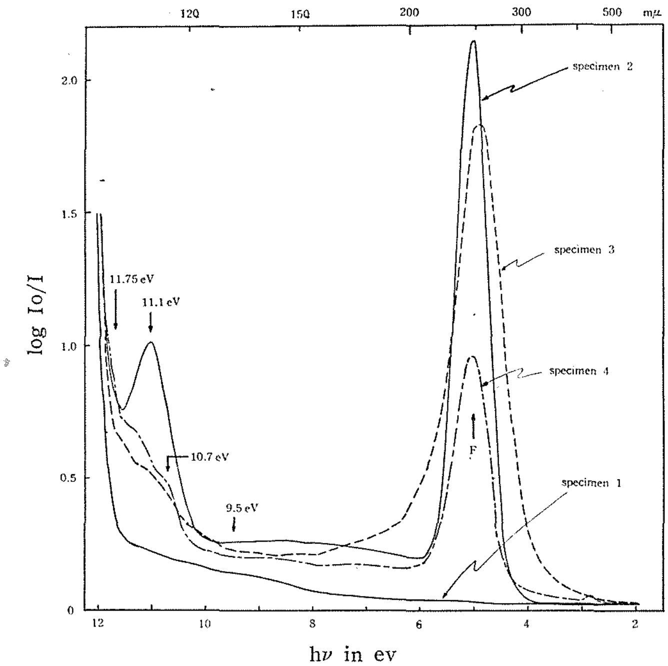

Fig. 1 Absorption spectra of irradiated LiF crystals (measured at room temperature). Specimen 1 : unirradiated crystal, 2 : irradiated with Van de Graaff electrons for 10 sec at $-70°C$, 3 : 2 min at 350°C, 4 : irradiated with γ-rays for 5 h at room temperature.

be produced proportionally in hight to F band as shown in Fig. 2. In specimens 3 and 4, however, a composite shoulder was observed and seems to consist of at least two bands at 11.1 and 11.75 ev. The much longer wavelength components were seen faintly at about 10.7 and 9.5 ev. They became also appreciable in specimen 2 when it was exposed to F light of 2537 Å (Fig. 3). Their intensities depend sensitively on histories of sample treatment and differ from specimen to specimen. Figs. 3 and 4 show the effect of light bleaching of F band in irradiated LiF crystals.

The width of each band at 5 ev in Fig. 1 suggests that specimens 3 and 4 contain other absorption components overlapping on F band. They appeared strongly when the specimens were exposed to F-light as seen in Fig. 4 and correspond to

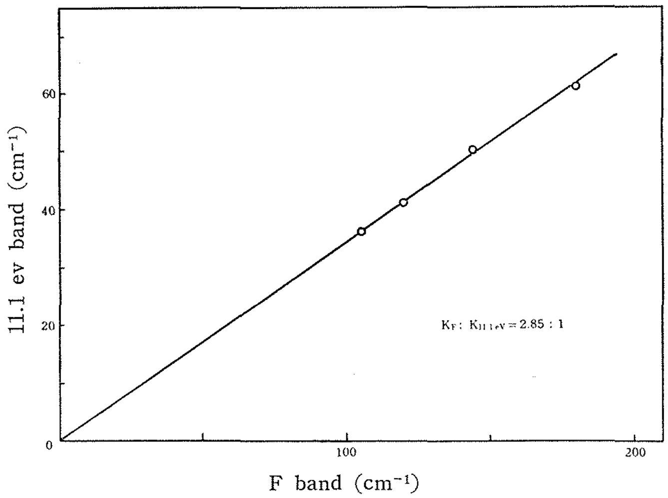

Fig. 2 The relation of absorption constants between F and 11.1 ev bands in LiF crystals irradiated with electrons at $-70°C$.

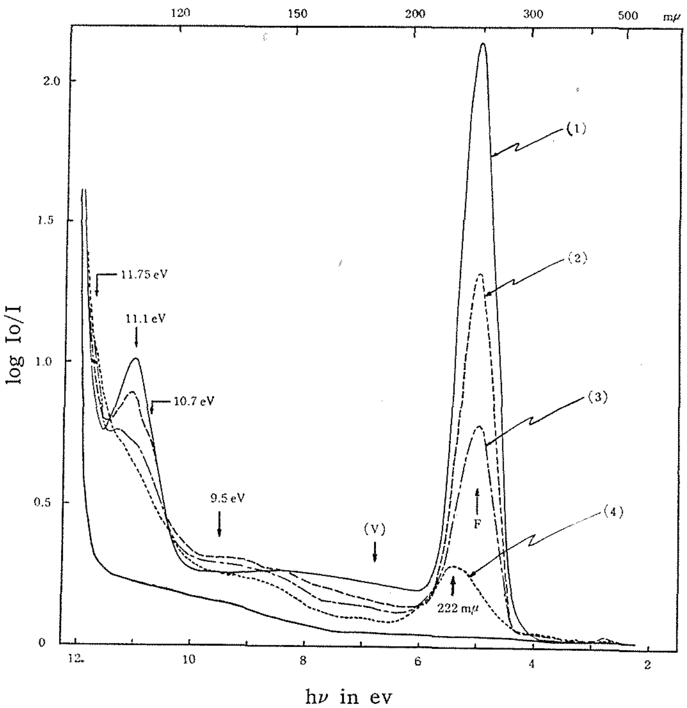

Fig. 3 Bleaching of F band in irradiated LiF crystal.

Curve (1) : *specimen 2 in Fig. 1,* (2) : *bleached* 3 h *with F light,* (3) : 3+3.5 h, (4): 3+3.5+5 h.

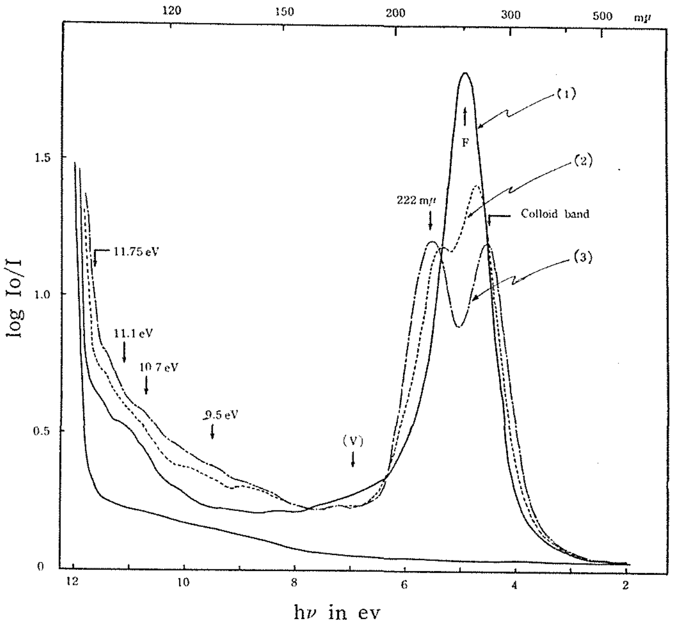

Fig. 4 Bleaching of F band in irradiated LiF crystal. Curve (1) : specimen 3 in Fig. 1, (2) : bleached 8 h with F light, (3) : 8+40 h.

222 mμ band and colloid band at 270 mμ as reported by Pringsheim *et al*[1]. It was found that when specimen 2 was bleached with F light the band at 11.1 ev decreased and the absorption near 11.75 ev increased as 222 mμ appeared, as seen in Fig. 3. Thus the existence of 222 mμ band is considered to have close relations with 11.75 ev band. The fact that the absorption shoulder at the tail of fundamental band consists of two bands at 11.1 and 11.75 ev in specimens 3 and 4 supports this speculation, because 222 mμ band is contained in both specimens immediately after irradiation with γ-rays or electrons. 222 mμ band is considered to be produced thermally from F band in specimen 3 or through destruction of F center by γ-rays in specimen 4 because the prolonged irradiation with γ-rays produces F centers in its early stage and destructs them concurrently in its late stage.

The behavior of 11.1 ev band reminds us of β band[3], but its separation from the lst exciton band* exceeds 1.5 ev and the appearance of 11.75 ev and 222 mμ bands accompanying the irradiation with F light made the analysis difficult. Therefore, further experiments are required to confirm the nature of 11.1 ev band. With the assumption that the concentration of 11.1 ev center is equal to F center, the oscillator strength of the band is estimated to be about 0.25 by using 0.82 of F center oscillator strength[4].

As seen in Fig. 3, a broad absorption from 6 to 8.5 ev (curve 1) disappeared with exposure to F light and is considered tentatively as a V band. As for the nature of 222 mμ band our knowledge has been meager. Now in this experiment

* The writer found the position of the lst exciton peak of LiF to be at 12.7 ev at room *temperature by measuring the reflection spectrum*[5].

it appeared strongly in specimen 3 (Fig. 4). Having been quenched to room temperature immediately after the electron bombardment at 350°C, specimen 3 is likely to contain many defects frozen in crystal. Then it is reasonable to consider that electrons released from F centers by the irradiation with F light are trapped in some kind of the defects to form 222 mμ centers. In fact, in specimen 2 irradiated with electrons at -70°C, the rate of change from F to 222 mμ band is much smaller than in specimens 3 and 4.

Finer experiments and quantitative analyses are now in progress.

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